REMARKS

I. Status of the Claims

Claims 7, 10, and 20-26 are pending. Claims 7 and 23-26 have been amended to more particularly point out and distinctly claim the subject matter Applicants regard as their invention. Support for the amended claims can be found in the specification and claims as originally filed. No new matter has been added.

II. Rejection Under 35 U.S.C. § 112

The Examiner has rejected claims 7, 10, and 20-26 under 35 U.S.C. § 112, second paragraph, as allegedly indefinite for failing to particularly point out and distinctly claim the subject matter regarded as the invention. *See* Office Action at 2-3.

The Examiner alleges that claim 7 is indefinite because it is "unclear as to whether the second section is altered such that its properties are different from the properties of the first section and then 'further alloyed with an easily diffusible element' or if the properties of the second section are altered by alloying with the easily diffusible element." Office Action at 2.

Applicants disagree and submit that previously pending claim 7 clearly defined and distinctively claimed Applicants' invention. To expedite prosecution, however, claim 7 has been amended to recite "an adjacent second section having a second set of properties which have been altered from the first set of properties by alloying the second section with an easily diffusable element." Applicants respectfully submit that amended claim 7 is not indefinite and request reconsideration and withdrawal of this rejection.

The Examiner asserts that claim 23 is indefinite because "[i]t is unclear whether the distal end having at least one altered property is in addition to the second section having altered properties . . . or if the distal end . . . is the second section." Office Action at 2.

Applicants disagree and submit that previously pending claim 23 clearly defined and distinctively claimed Applicants' invention. To expedite prosecution, however, claim 23 has been amended to recite "the second section of the superelastic member having the altered properties comprises a distal end of the superelastic member." Thus, the distal end is clearly defined as a part of the second section having the altered properties. Accordingly, Applicants respectfully request reconsideration and withdrawal of this rejection.

The Examiner also asserts that the limitation "the section" recited in claims 24 and 26 is indefinite because it is unclear whether the limitation is referring to the distal end or the second section. Office Action at 3.

Applicants disagree. However, to expedite prosecution, claims 24 and 26 have been amended to instead recite the "distal end." Accordingly, Applicants respectfully request reconsideration and withdrawal of this rejection.

III. <u>Rejection Under 35 U.S.C. § 102</u>

The Examiner has rejected claims 7, 10, and 22-26 under 35 U.S.C. § 102(e) as allegedly anticipated by Japanese Patent No. JP 04-187159 to Yamauchi et al. ("Yamauchi"). *See* Office Action at 3-4. Applicants respectfully disagree and traverse this rejection for at least the following reasons.

To establish the anticipation of a claim, the Examiner must show that <u>each element</u> of the claim at issue is found, either expressly or under the principles of inherency, in a single prior art reference. *Minnesota Mining & Mfg. Co. v. Johnson & Johnson Orthopaedics, Inc.*, 976 F.2d 1559, 24 U.S.P.Q.2d 1321 (Fed. Cir. 1992) (emphasis added). Further, "[t]he identical invention must be shown in as complete detail as is contained in the . . . claim." *Richardson v. Suzuki*

Motor Co., 868 F.2d 1226, 1236, 9 U.S.P.Q.2d 1913, 1920 (Fed. Cir. 1989) (citations omitted). *See also* M.P.E.P. § 2131.

The Examiner asserts that Yamauchi teaches an elongated medical device comprising a superelastic member formed from a nickel-titanium alloy, and further asserts that the elongated medical device of Yamauchi has a first, top end section with a first set of properties and a second, base section having a second set of properties that have been altered from the first set of properties. Office Action at 3. The Examiner further asserts that the second section may be alloyed with carbon and the altered properties of the base section "include reduced superelasticity." Office Action at 3. The Examiner also asserts that "[t]he distal end of the superelastic member has at least one property that is altered from its original state through temperature treatments, and that property is also reduced superelasticity." Office Action at 3. Finally, the Examiner asserts that the entire superelastic member of Yamauchi has properties that are altered from their original state and has a total length greater than 3 cm. Office Action at 4.

Applicants disagree. The Examiner's above assertions are technically unfounded and mischaracterize the teachings of Yamauchi. As shown above, Yamauchi does not teach each of the elements recited in the present claims.

Claim 7 recites, *inter alia*, a first section with a first set of properties and an adjacent second section having a second set of properties which have been altered from the first set of properties by alloying the second section with an easily diffusable element. Yamauchi does not teach this limitation.

Contrary to the Examiner's assertions, Yamauchi teaches that the properties of the base section and the apex are altered by heat treating each section at a different temperature. *See* Yamauchi, English abstract. Yamauchi does not teach that the base section has properties altered

by alloying the base section with an easily diffusible element. In fact, Yamauchi does not even teach that the base section and apex section are made of different materials.

The Examiner's assertion that Yamauchi teaches altering the properties by reducing the superelasticity of both the base section and the apex section of the medical device are wholly unsupported by the disclosure of Yamauchi. Yamauchi teaches that the heat treatment steps provide "twist transmitting properties" to the base part and flexibility to the apex. *See* Yamauchi, English abstract. Improving the twist transmitting properties suggests an increase in the ability of the material to transfer the torque applied to the base section, i.e., increasing the stiffness. In fact, one skilled in the art would recognize that the heat treatment steps disclosed by Yamauchi actually <u>increase</u> superelasticity. In this regard, Duerig et al. disclose the effects of heat treatment on superelastic alloys. *See* Duerig et al., "An Engineer's Perspective of Pseudoelasticity," *Engineering Aspects of Shape Memory Alloys*, pp. 369-393 (1990) (herein referred to as "Duerig"). Duerig teaches that heat treatment retains the ability to stress induce martensite and strengthens the austenitic phase. Duerig at 382-383. In addition, lower heat treatment temperatures increase superelastic stiffness. Duerig at 385. Therefore, the heat treatment of Yamauchi would be understood by the skilled artisan to increase superelasticity in the base and apex sections.

Further, the Examiner acknowledges that the entire elongated device of Yamauchi is altered from its original state. *See* Office Action at 4. Based on this teaching alone, Yamauchi does not anticipate the present claims, which recite, *inter alia*, a first section with a first set of properties and an adjacent second section having a second set of properties which have been altered from the first set of properties. Assuming for the sake of argument that Yamauchi's apex is considered a first section having a first set of properties, the base section never exhibits a

second set of properties which have been altered from the first set of properties, because both sets of properties are altered.

Because Yamauchi does not teach each and every element recited in the present claims, Yamauchi does not anticipate the present claims. For at least the foregoing reasons, Applicants respectfully request reconsideration and withdrawal of the rejection.

IV. Rejection Under 35 U.S.C. § 103

The Examiner has also rejected claims 20 and 21 under 35 U.S.C. § 103(a) as allegedly unpatentable over Yamauchi. *See* Office Action at 4-5.

In order to carry the initial burden of establishing a prima facie case of obviousness, the Examiner must show that the prior art reference teaches or suggests all of the claim limitations. See M.P.E.P. § 2143. In addition, there must be some suggestion or motivation to modify the reference. M.P.E.P. § 2143.

The Examiner asserts that Yamauchi discloses a superelastic member that is alloyed with carbon, an easily diffusible element and acknowledges that Yamauchi does not teach the alloying of the second section with hydrogen or oxygen, as recited in the present claims. *See* Office Action at 4. The Examiner, however, asserts that it would have been obvious to one skilled in the art to have used hydrogen or oxygen rather than carbon "because such a modification would have been considered a mere design consideration which fails to patentably distinguish over Yamauchi." Office Action at 4-5.

Applicants disagree. There is absolutely no teaching or suggestion in the prior art to substitute hydrogen or oxygen for carbon in the device of Yamauchi. The prior art does not even teach that oxygen and hydrogen diffuse into nickel-titanium alloys. In fact, Yamauchi does not even recognize that carbon alters the properties of the nickel-titanium alloy. Rather, Yamauchi

teaches a heat treatment that alters the properties of the material. *See* Yamauchi, English abstract. Accordingly, the prior art does not teach or suggest each of the limitations recited in the present claims.

Furthermore, the Examiner has improperly used Applicants' own specification for any suggestion that oxygen and hydrogen can alter the properties of nickel-titanium alloy. Based on the teachings of Yamauchi, one skilled in the art would not have been motivated to substitute hydrogen or oxygen for carbon because Yamauchi neither teaches nor suggests that any element other than carbon may be used.

For at least the foregoing reasons, Applicants respectfully request the reconsideration and withdrawal of the rejection.

V. Conclusion

In view of the foregoing amendments and remarks, Applicants respectfully request reconsideration and reexamination of this application and the timely allowance of pending claims 7, 10 and 20-26.

Please grant any extensions of time required to enter this response and charge any additional required fees to our Deposit Account No. 06-0916.

Respectfully submitted,

FINNEGAN, HENDERSON, FARABOW,
GARRETT & DUNNER, L.L.P.

Dated: May 9, 2006

By: Michele C. Bosch
Michele C. Bosch
Reg. No. 40,524

Attachment: Duerig et al., "An Engineer's Perspective of Pseudoelasticity," *Engineering Aspects of Shape Memory Alloys*, pp. 369-393 (1990).

Engineering Aspects of
Shape Memory Alloys

T W Duerig, BS, ME, PhD
Technical Director, Raychem Corporation, Menlo Park, California, USA

K N Melton, BA, PhD
Director of Research and Development, Raychem Corporation, Swindon, UK

D Stöckel, Dip Ing, PhD
Technical Marketing Manager, Raychem Corporation, Menlo Park, California, USA

C M Wayman, BS, MS, PhD
Professor of Materials Science and Engineering, University of Illinois, Urbana, Illinois, USA

Butterworth–Heinemann
London Boston Singapore Sydney Toronto Wellington

PART OF REED INTERNATIONAL P.L.C.

First published 1990

British Library Cataloguing in Publication Data

Engineering aspects of shape memory alloys.
1. Alloys. Shape memory effects
I. Duering, T. W.
669.94
ISBN 0-750-61009-3

Library of Congress Cataloging-in-Publication Data

Engineering aspects of shape memory alloys / edited by T.W. Duerig.
p. cm.
Includes bibliographical references and index.
ISBN 0-750-61009-3
1. Alloys--Thermomechanical properties. 2. Shape memory effect.
I. Duerig, T. W.
TN6980.E546 1990
669'.9--dc20 90-2104
CIP

Printed and bound in Great Britain by Courier International Ltd, Tiptree, Essex

Introduction

It has now been over 50 years since the first observations of shape memory, and over 20 years since people first began to find applications for the effect. Certainly many people believe that practical application has progressed much slower than expected: when inventive people first observe the effect they immediately begin to conjure ideas for its application, amazed that it has been known for so long by the scientific community and is yet nearly unknown to design engineers. Shape memory has even become famous as "a solution looking for a problem".

But this reputation is unfair if one considers that the entire technology is new. These are not simply new alloys of steel or titanium, but represent an entirely new philosophy of engineering and design. The most fundamental property descriptors are different: yield strength, modulus, and ductility are replaced by stress rate, recovery stress and M_s. Moreover, product designs using shape memory are generally not evolutionary, but revolutionary in nature. One can hardly expect large industries to immediately convert basic product designs to shape memory. In fact progress has been impressive. At the time of writing, it is estimated that the worldwide business in shape memory exceeds 30 million US dollars, and is growing at over 25% per year. Product diversity is also most impressive, including fine medical wires, electrical switches, eyeglass frames, appliance controllers, pipe couplings and electronic connectors.

Still, it is clear that the technology lags behind the science. The origin and mechanism of shape memory are now well understood, but many of the engineering aspects are not. The purpose of this book is to extend our understanding of shape memory by defining terms, properties and applications. It includes tutorials, overviews, and specific design examples - all written with the intention of minimizing the science and maximizing the engineering aspects. Although the individual chapters have been written by many different authors, each one of the best in their fields, the overall tone and intent of the book is not that of a proceedings, but that of a textbook. There has been a concerted editing effort to unify terms, avoid duplication, and fill gaps.

Shape memory applications can generally be divided into four categories: free recovery, constrained recovery, work production (actuators) and superelasticity. These groupings are made according to the primary function of the memory element, but are useful in defining common product screening criteria, pitfalls and engineering design parameters. We define the groups as follows:

An Engineer's Perspective of Pseudoelasticity

T.W. Duerig and R. Zadno
Raychem Corporation
Menlo Park, CA

The fourth type of shape memory event or application is different from the previous three in the sense that it is completely isothermal. In the most general sense, any non-linearity in a stress-strain curve during unloading can be referred to as pseudoelasticity. Typical examples are shown in Figures 1 and 2. Figure 1 shows a small non-linearity which can

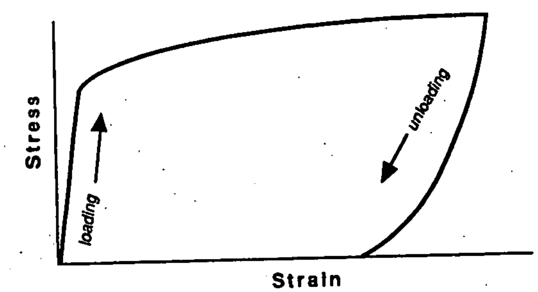

Figure 1: An idealized stress-strain curve showing generic pseudoelasticity, defined by a non-linearity during unloading.

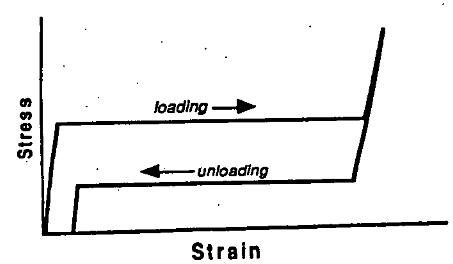

Figure 2: Idealized superelasticity, showing a clear unloading plateau and an extremely large elastic range.

present very real problems to engineers trying to base designs on a constant elastic modulus, but as will be shown, also provides one of the most important benefits of shape memory coupling devices. Figure 2 shows a more useful aspect of pseudoelasticity: under certain circumstances, a pseudoelastic metal can be deformed more than 10 times as far as a conventional metal and still completely springback to its original undeformed shape. Because of the enormous amount of elastic deformation available in these metals, this second type of pseudoelasticity is often referred to as "*superelasticity*", and represents one of the most useful manifestations of the shape memory effect.

The terms superelasticity and pseudoelasticity have often been used interchangeably. For the purposes of this paper, pseudoelasticity will be used as the more general term, referring to any non-linearity during unloading. Superelasticity will be a more specific term, used to describe pseudoelastic materials that show a plateau during unloading. Since tensile curves are often not as clearly defined as in Figure 2, we use the presence of an inflection point during unloading as evidence of a plateau.

In this paper we will overview the various causes of pseudoelasticity, discuss some of its mechanical aspects, and then look at the various ways to develop the effect. In general the emphasis will be on Ni-Ti since that remains the preferred superelastic alloy. Although the use of superelastic materials looks at first to be very appealing in many designs, there are two factors that have significantly reduced the scope of application: an extreme temperature dependence of some of the key mechanical characteristics and some comparatively complicated fatigue effects. The first of these will be discussed in some detail in this paper, while the second will be treated in detail in the following paper.

1. The Mechanisms of Pseudoelasticity

Pseudoelasticity can be caused by either twinning or by a stress induced phase transformation. Though both mechanisms will be considered in this section, the emphasis in subsequent parts will be with transformational pseudoelasticity since practical *super*elasticity has only been achieved through this mechanism.

1.1 Twinning Pseudoelasticity

Twinning pseudoelasticity is caused by the reversible motion of twin boundaries. In materials that are deformed by either the formation of twins or by the motion of twin boundaries, it is often the case that the positions of the twins in the deformed state are not stable, and that there is a driving force causing them to return to their original positions during unloading[1]. We will look at a few examples of such phenomena.

Figure 3 shows a typical tensile curve of Ni-Ti in the austenitic phase, well above M_d so one can be sure that no transformational effects are involved. In this case, the material is known to deform by mechanical twinning[2]. This process is different from conventional twinning in that it leaves the lattice improperly ordered and thus in a higher energy state. This is called *pseudotwinning*, and might, rigorously speaking, be called a phase transformation. When the stress is removed, some of the twins will shrink or even disappear in order to return the preferred lattice ordering.

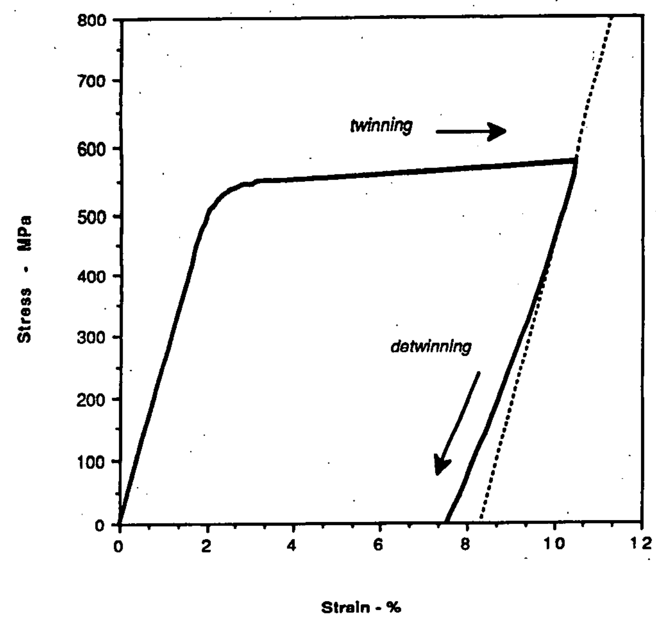

Figure 3 A room temperature stress strain curve of a NiTiFe shape memory alloy showing pseudoelastic behavior due to pseudotwinning. M_d in this alloy is -30°C, so no martensitic transformation is involved.

This provides a springback strain above and beyond the normal elastic effects - represented by the light line tangent to the unloading line in Figure 3. Although the pseudoelastic effect is small, it is of great practical importance in couplings and fasteners since it reduces the apparent modulus of the installed Ni-Ti device. Reducing modulus creates what is often called a "live" joint, meaning that it is better able to compensate for differential thermal expansion and other small motions tending to separate the recovered part from the substrates being joined. Note also that we can define three moduli for the unloading portion of Figure 3: a tangent modulus at the onset of the unloading, a tangent modulus at zero load (always lower than the first), and a secant modulus (simply connecting the starting and finishing points) - which of these is the most relevant depends upon its intended use. Figure 4 shows some other interesting aspects of pseudoelasticity that concern cyclic loadings. The most obvious is that reloading does not follow the same path as unloading, so that a strain hysteresis develops. Secondly, though less obvious without careful data analysis, the unloading secant modulus monotonically decreases as the deformation in increased[3].

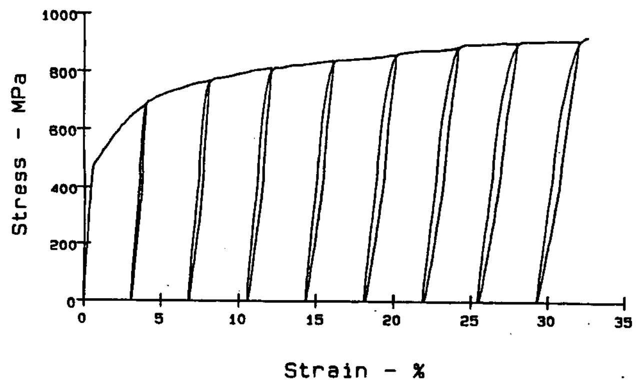

Figure 4 Repeated loading and unloading cycles of the same alloy shown in Figure 3 illustrate that pseudoelasticity can result in a hysteresis, which increases in width with total strain.

The martensitic phase of Ni-Ti also shows twinning pseudoelasticity, as shown in Figure 5. In this case deformation proceeds by the motion of martensite twin boundaries. Although the motion does not cause disorder, there nevertheless appears to be a driving force for the twins to return to their original positions when the stress is removed. It is not clear whether this is due to residual stresses, a desire for accommodation dislocations in the twin boundaries to maintain an even spacing, or is

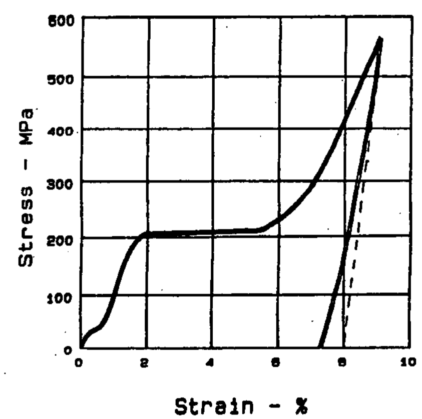

Figure 5 Twinning pseudoelasticity in NiTiFe martensite. In this case deformation was at -196°C while A_s is -100°C. (The first small inflection at 0.5% strain is due to a reorientation of the R-Phase.)

related to reducing the tapered portion of martensite plates[4]. Martensitic pseudoelasticity appears to have no constructive value, but does play an important role in design in that it complicates calculations of springback and the compliance of a device.

The previous two examples of twinning pseudoelasticity were small effects with no direct practical application. Larger twinning superelastic effects are observed in many systems such as AuCu [5,6] and InTl[7]. In the case of AuCd, the martensite structure is orthorhombic, and undergoes mechanical pseudotwinning. Unlike the austenitic phase of Ni-Ti, proper variant selection of the pseudotwins in AuCd can result in springback strains of several percent. This enhanced elasticity has also been called *ferroelasticity* due to certain similarities with magnetism[5]. One interesting aspect of this, however, is that aging at room temperature while in the deformed state will lock-in that shape and prevent superelastic springback[8]. This aging effect is due to a reordering of the pseudotwins, bringing them back to their more stable configuration of atomic order. Due to the chemical make-up of these special alloys there has not been a substantial effort to commercialize them.

1.2 Transformational Superelasticity:

For the purposes of this paper, we will only discuss transformational pseudoelasticity in its fully evolved form: superelasticity. Transformational superelasticity requires that a stress induced transformation occurs, usually stress inducing a martensitic phase from an austenitic. This is illustrated in Figure 6. The austenitic phase is

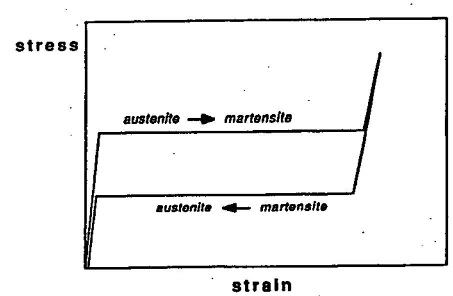

Figure 6 Superelasticity results when martensite must be stress induced, and when austenite again becomes the stable phase when the stress is removed. The plateaus themselves are caused by the ability of martensite to accommodate the applied stress by selecting those variants most favorably inclined.

stable before the application of a stress, but at some critical stress the martensite becomes the more stable, causing yielding and a stress plateau. The plateau is caused by the ability of martensite to form in several different variants just as in the case of shape memory, the

difference being that in this case the variants are selected during the transformation itself instead of through the progressive consumption of some variants by others. The details of deformation along the stress induced plateau will be treated later in more detail; now, it is enough to observe that at some strain the structure becomes completely martensitic and the stress again begins to increase in a linearly elastic way, but this time according to the martensitic modulus. Since the martensite is only stable because of the applied stress, the austenite structure again becomes stable during unloading, and as discussed in previous sections, the original undeformed shape must be returned. Thus the reverse transformation causes an unloading plateau, but at a lower stress level due to the transformational hysteresis.

Transformational superelasticity can only be realized if the temperature of the material is below M_d and above A_s. If the temperature exceeds M_d the martensite cannot be stress induced; if the temperature is below A_s the stress induced martensite will remain stable during unloading and again no unloading plateau will be observed. In fact for full superelasticity we require the application temperature to be above A_f. The details of this temperature dependency are well summarized in Figure 7, and will be examined in more detail in the section 2.2.

Figure 6 showed an example of superelastic behavior in Ni-Ti, the most commonly used alloy. Significant superelasticity can also be found in Cu-based memory alloys. In the case of Cu-Al-Ni, large strains have only been

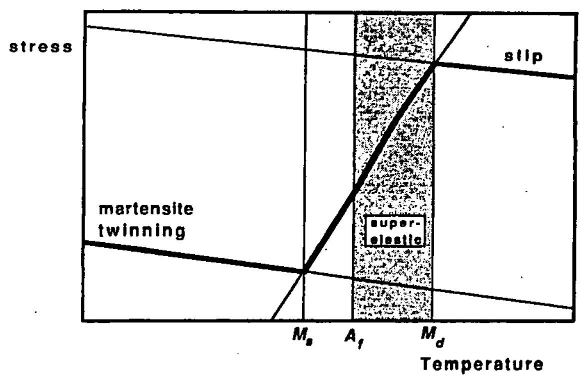

Figure 7 A stress-temperature phase diagram illustrating the temperature range in which superelasticity can be found. The heavy line represents the variation in yield stress usual to shape memory alloys. Below M_s, deformation occurs by martensite twinning; between M_s and A_f, the martensite is stress induced, but once induced, is stable; between A_f and M_d the stress induced martensite becomes unstable during unloading and superelasticity is observed; above M_d the deformation is due to slip since martensite can no longer be stress induced.

reported in single crystals[9], where superelasticity is enhanced by successively stress inducing different martensite structures (Figure 8).

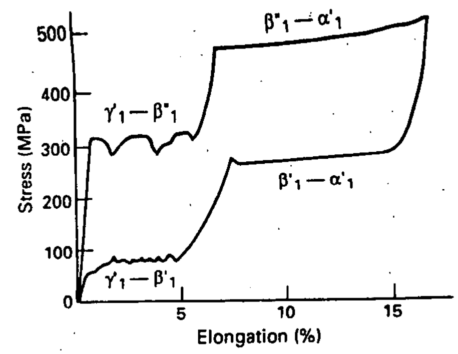

Figure 8 Single crystals of CuAlNi are known to exhibit extremely large superelastic strains (nearly 20% in certain crystallographic directions). These strains are the result of successive martensitic transformations from a DO_3 austenite. (Figure from Otsuka and Shimizu[9]).

Perhaps the most interesting aspect of this sequence is that one of the stress induced martensites (β_1') leads to a hysteresis-free superelasticity[10]. Still, polycrystalline Cu-Al-Ni alloys tend to be inherently brittle, subject to fatigue and to have much smaller superelastic strains (on the order of 1%)[11]. For these reasons, they are not particularly interesting from an engineering point of view. Larger transformational superelasticity (on the order of 5%) can be found in polycrystalline Cu-Zn[12,13] and various ternaries based on that system[14], best known of which is Cu-Zn-Al[15,16]. There are currently no superelastic applications of Cu-Zn-Al, so the engineering principles are less well known than in the Ni-Ti system.

2. A Mechanical description of superelasticity:

Since the stress-strain curve shown in Figure 2 is unusual, it is necessary that several new physical descriptors be defined - these are shown in Figure 9: the loading plateau stress (σ_l), the unloading plateau stress (σ_u), the total deformation strain (ε_t), the permanent set or unrecovered strain (ε_p), and the stored energy (E) (defined as the area under the unloading curve). Figure 9 is very clearly defined, but this is not always the case; the plateaus can often be difficult to clearly distinguish, particularly in

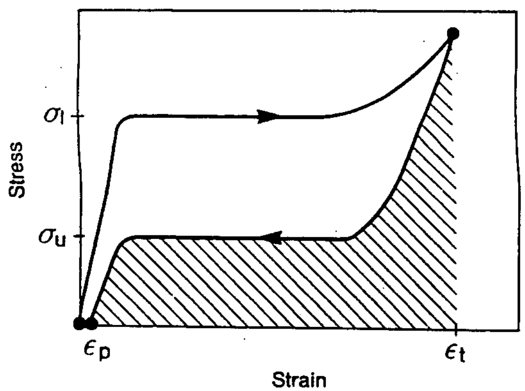

Figure 9 A schematic superelastic stress-strain curve defining various key mechanical descriptors: the loading stress - σ_l, and unloading stress - σ_u, the total strain - ε_t, and the permanent set - ε_p. The two plateau stresses are defined by the inflection points, the springback strain (not shown) is defined by the difference between the total and plastic strains, and the stored elastic energy is defined by the area under the unloading curve (shaded).

polycrystalline Cu-based alloys, so it is necessary to define σ_l and σ_u in such a way as to be easily measured in ill-defined curves. The best definition appears to be to use the stress at which inflection occurs. The difference between σ_l and σ_u is the superelastic hysteresis, which is a direct consequence of the thermal hysteresis in the shape memory event, and can be quantitatively connected to the thermal effect through the stress rate from the Clausius-Clapeyron equation[1,15].

2.1 Strain dependencies

The first mechanical aspect of superelasticity to be discussed is the dependence of the above superelastic properties upon the total deformation strain - ε_t. Clearly the permanent set (ε_p) should increase as the total strain exceeds some critical value and slip begins to contribute to the overall deformation. Figure 10 shows a typical relationship, with no measurable permanent set at strains below about 8%, and with permanent set increasing from that point on. The largest recoverable strain observed in polycrystalline Ni-Ti is 11% - this includes both the elastic and superelastic contributions. Figure 11 shows a second important effect of the total strain. Although the loading plateau of course remains constant, the unloading plateau is decreased as the total deformation in increased. This means, in effect, that the stress hysteresis increases as the material is deformed. One can easily imagine that some materials are

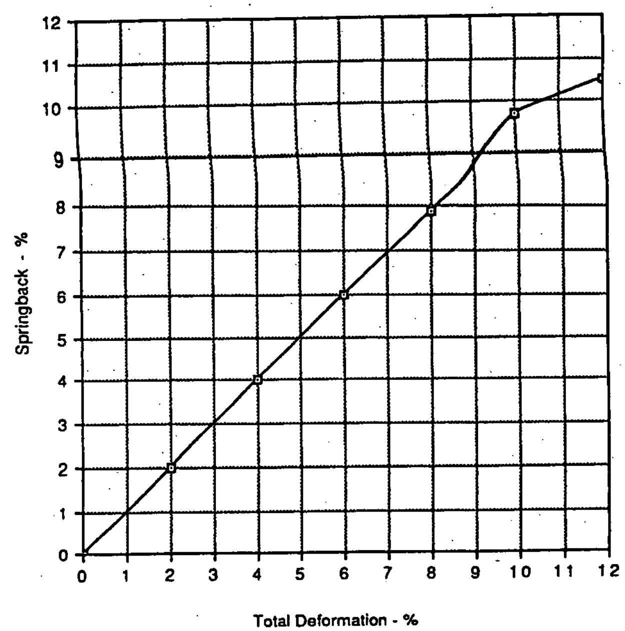

Figure 10 The dependence of springback strain (ε_t-ε_p) upon the total tensile deformation. The results are for a Ni-Ti wire with 50.8% Ni after cold working 40% and annealing at 375°C for 30 minutes.

superelastic only after small deformations. One curious but important implication of Figure 11 is that one does not necessarily store more energy by deforming further - increasing deformation beyond 6% increases springback, but the ensuring reduction in stiffness is substantial and can actually reduce the springback energy. This same effect has been observed in Cu-Zn-Al[17].

2.2 Temperature dependencies

As pointed out earlier, the extreme temperature dependency of superelasticity is one of the two factors most limiting to its use. This is shown quantitatively in Figures 12 and 13. Figure 12 shows that very low ε_p values can only be obtained over a 60°C temperature range. Below this ideal window, recovery during unloading is incomplete but heating after unloading will complete recovery. Above the ideal window the temperature approaches M_d and the applied deformation can no longer be accommodated without some dislocation movement; in this case, heating

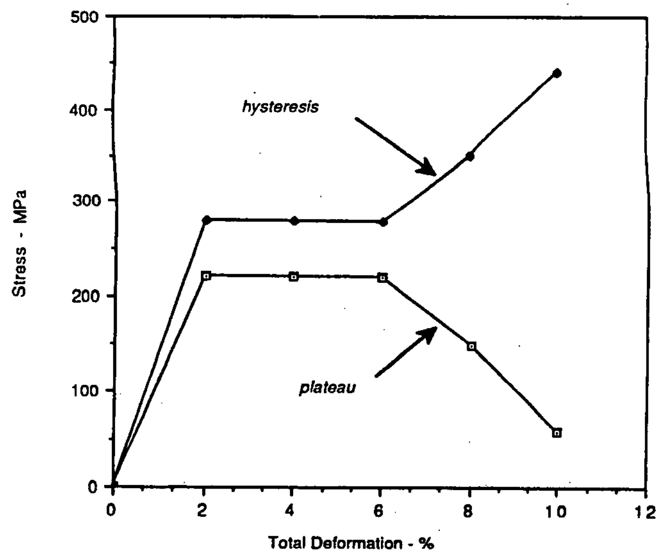

Figure 11 The dependence of the unloading plateau stress upon total deformation in the same wire described in Figure 10.

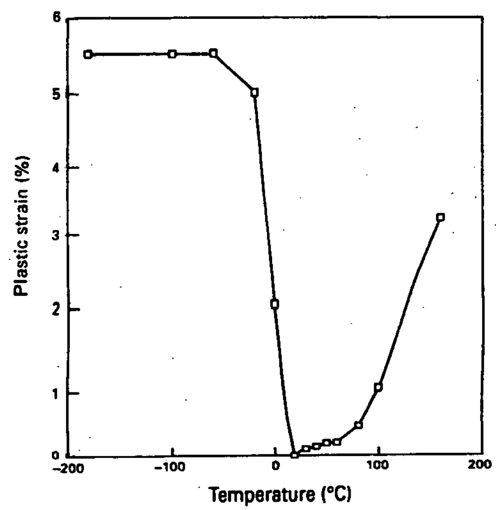

Figure 12 The temperature dependence of plastic strain, or permanent set, after an 8% tensile deformation. The wire was Ni-Ti with 50.8 at. % Ni and was cold worked 40% and annealed at 375 for 30 minutes beforetesting.

after unloading should cause no additional recovery. As we will see in section 3, there are a variety of ways to move the ideal window to lower or higher temperatures, but windows wider than 80°C have not as yet been observed in Ni-Ti.

Figure 13 shows a second aspect of this temperature dependency: the effect of temperature upon σ_l and σ_u. As the temperature increases, so does the difference between ambient temperature and M_s, and so do the two plateau stresses. The rate of increase is linear and follows the Clausius-Clapeyron equation. Typical values for the rate of increase, or stress rate, range from 3 to 20 MPa/°C in superelastic Ni-Ti alloys[18]. This increases is extremely significant in design even when the expected temperature changes are small. In the example shown in Figure 13, one would expect the unloading stiffness to more than double between room temperature and body temperature. It is therefore essential that medical product testing be done at body temperature.

One should be aware that the phase transformation has a rather high latent heat of transformation - about 5 cal/g in Ni-Ti, but strongly dependent upon M_s[19]. Thus although we frequently say that the superelastic event is isothermal, this is often not the case due to self-heating in the specimen. As strain rates increase, and conditions become

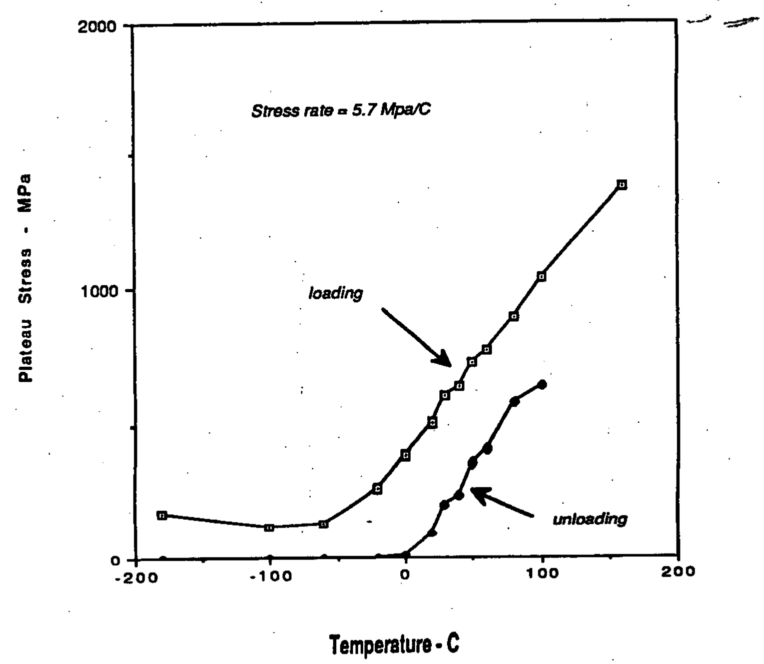

Figure 13 The temperature dependence of the plateau stresses inthe same wire described described in Figure 12. The stress increase follows the Claussius-Clapeyron equation.

more adiabatic, this effect can become quite substantial, often causing a temperature rise upon deformation of well over 5°C (and of course a similar temperature drop upon unloading). This thermal effect has been observed in both Ni-Ti[20] and in Cu-Zn-Al[21]. One result of this is to introduce some apparent strain rate effects.

2.3 Energy storage

The storage of large amounts of elastic energy is, more often than not, the primary driving force for using a superelastic material. Elastic energy is defined as $\int \sigma d\varepsilon$, or the area under the unloading portion of the stress-stain curve (as shown in Figure 9). Table I compares typical elastic energy storing capacities for some of the better known spring materials with that of superelastic Ni-Ti and Cu-Zn-Al. The advantage of superelasticity is clear. Still, one must be aware that these values must be derated for fatigue effects, and as will be discussed in the next paper, the derated values for Ni-Ti and Cu-Zn-Al are far less favorable than those shown in Table I. The values for Ni-Ti and Cu-Zn-Al shown in the tables are approximate (but very conservative) numbers for room temperature pseudoelasticity - at 50°C, it would be possible to significant better these figures. It should also be noted that the numbers for Cu-Zn-Al may not represent a maximum since a systematic and complete analysis has never been done. These are numbers calculated from typical literature data[13,15].

Table I: Comparison of the Elastic Energy Storage Capacity of Various Spring Materials.

Material	Maximum Springback Strain	Stored Energy
Steel	0.8%	8. Joules/cc
Titanium	1.7%	14. Joules/cc
Ni-Ti	10.0%	42. Joules/cc
Cu-Zn-Al	5.0%	14. Joules/cc

2.4 Detailed stress and strain analysis

The stress applied by a pseudoelastic spring is not dependent upon deflection, but on temperature; exactly opposite to a conventional spring. For many applications, this is one of the most appealing features of superelasticity: one can apply a constant stress over a very wide range in strain. But again one must be careful. The curves shown in Figures 2 and 9 are tensile stress-strain curve; torsional or bending curves would look substantially different due to the unusual non-linear strain distribution across the cross-section (common bending and torsional models assume elasticity to derive the strain distribution). Absolutely flat tensile stress-strain curves such as shown in Figure 2 are quite easily produced in Ni-Ti, but the same material will show substantial work hardening in bending and torsion[22-24]. This is illustrated in Figure 14, where actual tensile properties of a superelastic Ni-Ti alloy are used in a finite

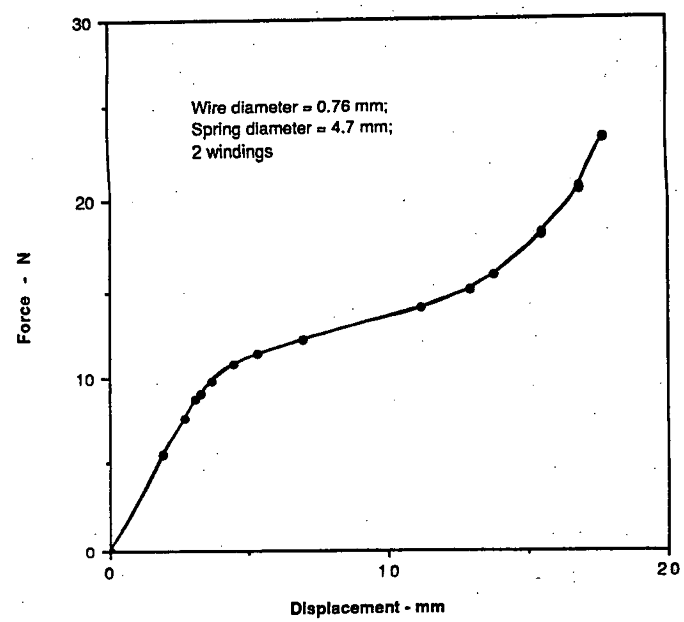

Figure 14: One complication of superelastic product design is that conventional bending and torsional formulae are no longer valid, and finite element analyses, though complicated, must be used. Shown is a numerical calculation of load-deflection in a helical spring using the program MARC, and actual data from an ideally superelastic (flat loading plateau) Ni-Ti alloy. It is impossible to achieve a flat loading plateau in torsion or bending.

element analysis of torsion.[24] Compressive properties too greatly differ from tensile even though strain distributions are uniform.[25]

Finally, it is worthwhile taking a closer look at what is occurring as deformation proceeds along the loading and unloading plateaus. As the engineering stress-strain curves can be perfectly flat in this region, one might wonder what the true stress-strain curves would look like - for many design approaches this information is essential. Traditionally one would assume a uniform change in the cross-sectional area and conservation of volume, then calculate the true stress-strain values from areas based on elongation. As is so often the case with these alloys, this approach is not successful. Deformation along the plateau occurs by the growth of Lüder's bands[25] - thus we do not have a uniform cross section, but locally necked regions which grow in length until they consume the entire gauge length. The area is either the deformed area or the undeformed - there is no in-between. As deformation proceeds, the integrated length of the necked regions grow linearly with strain until the

end of the plateau. So, in fact, the entire concept of true stress-strain and engineering stress-strain must be realigned to fit superelastic deformations.

3. Processing to produce and maximize superelasticity

Nearly all shape memory alloys are superelastic at some temperature. To be useful, the superelastic temperature range must be made as wide as possible, and must be centered around the application temperature. The process of shifting the window can be accomplished rather easily by the methods described in earlier chapters. Here we will predominately deal with methods used to maximize the window width, which directly results in reducing the permanent set. Because there is a great deal more data available for the Ni-Ti system than for the Cu-based, our examples will key upon Ni-Ti, but the principles involved are valid for all alloys.

There are four property modifications that will directly increase the width of the superelastic window:

1. Increasing austenitic strength: This has the effect of delaying the onset of dislocation movement, thereby increasing M_d and increasing the upper temperature bound for the superelastic window.
2. Decreasing the stress rate: Given a critical stress for the onset of dislocation movement, decreasing the rate at which stress will be increase will also raise M_d.
3. Decreasing hysteresis and/or increasing the steepness of the transformation: Both will tend to keep A_f closer to M_s and therefore further separated from M_d. One can also think of this in terms of decreasing the stress hysteresis, thereby ensuring an unloading plateau at lower temperatures.
4. Eliminating or suppressing the R-Phase: If the R-Phase transformation occurs above A_f, it will then be controlling of the point at which the window for complete superelasticity begins. This is actually of significant importance since the high strength conditions that normally show superelasticity also show an R_s above room temperature.

For the most part, the logic of each of the above four can be seen in Figure 7. Although all are important, the most important is the first. There are two practical methods of accomplishing this in Ni-Ti: cold working and age hardening. Since Ni-Ti alloys with less than 50.6 at.% Ni are stable[27], this clearly limits the use of the second approach to Ni-rich compositions. It should also be noted that it may not be possible to have the first without the second in Ni-rich alloys. We will now briefly discuss both approaches.

3.1 Cold worked superelastic Ni-Ti:

As has been discussed in earlier[27], Ni-Ti can be strengthened by cold working, but in order to preserve the ability to stress induce martensite the cold working operation must be followed by a recovery anneal. To illustrate these effects upon superelasticity, we will follow the behavior

of a Ni-Ti V alloy, though the same trends exist in the binary alloys. The reason for choosing this particular alloy is that it is stable, and allows us to ignore aging effects which could complicate the issue in the binary alloys.

As the annealing temperature is decreased, more cold work is retained and the austenitic phase is strengthened while ductility is reduced (illustrated in Figure 15). On this basis, one would then expect better

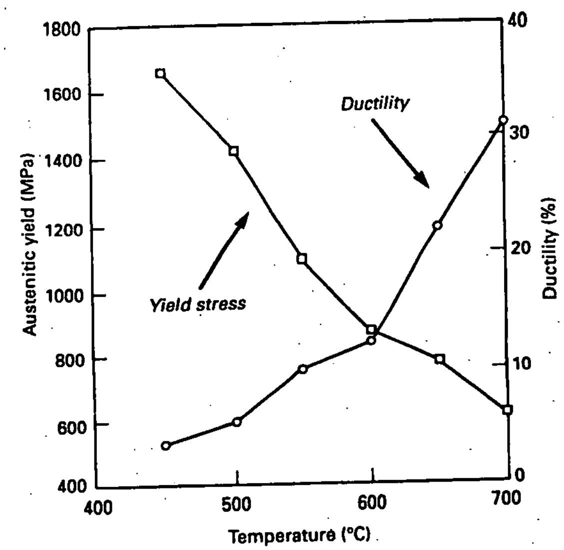

Figure 15 Strengthening response of a superelastic Ni-Ti-V wire after cold working 40% and annealing for 1 hour at the temperature shown on the ordinate.

superelasticity after lower temperature anneals. Figure 16 shows that the stress rate is rather dramatically reduced by lowering the annealing temperature, again indicating superior superelasticity. Figure 17 shows that M_s decreases as more cold work is retained; since A_f is below room temperature in all cases (Figure 17 shows the transformation temperatures under load - the unloaded values are roughly 15 degrees lower), we expect superelasticity at all cases. Also shown in Figure 17 is that the thermal hysteresis is decreased by increasing the annealing temperature, a factor favoring superior superelasticity after more complete anneals. Finally, we might expect higher superelastic stress plateaus after lower annealing temperatures since the difference between the application temperature and A_f is greater. The net effect of all these factors can be seen in figures 18 and 19. Lower annealing temperatures

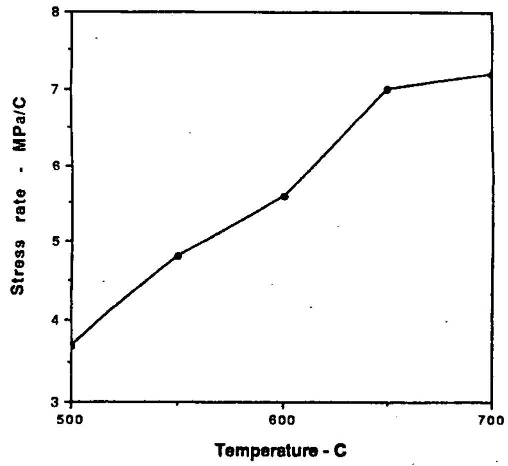

Figure 16 Stress rate is dramatically influenced by the amount of residual cold work. This trend of decreasing stress rate with increasing resistance to slip is common and quite powerful, but not fully understood. The alloy is as described in Figure 15.

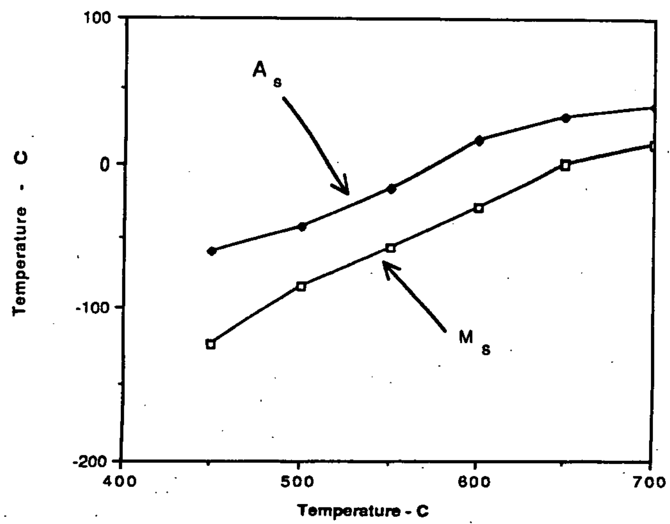

Figure 17 The transformation temperatures A_s and M_s measured mechanically at 150 MPa (the unloaded values would be less by an amount determined by the stress rate). The general trend of decreasing M_s with increasing residual cold work is usual in Ni-Ti alloys. The alloy is as described in Figure 15.

decrease permanent set after room temperature deformations (Figure 18) and increases the superelastic stiffness (Figure 19). We can see that the smaller thermal hysteresis found after the hotter annealing treatments manifests itself as a smaller stress hysteresis in Figure 19.

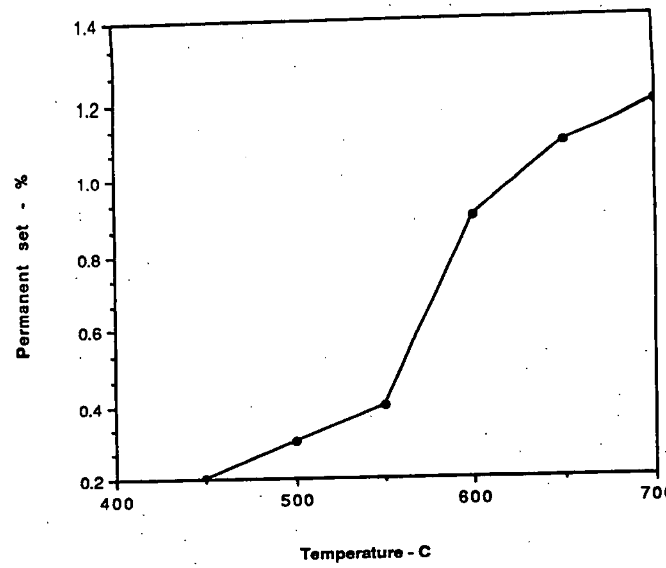

Figure 18 Permanent set (ε_p) after deforming 8.0% at 20°C is shown as a function of annealing temperature. The alloy is as described in Figure 15.

Thus decreasing the annealing temperature has every advantage in terms of superelasticity (lower permanent set, greater stiffness and greater energy storage capacity) but ductility is decreased as an exchange; the need to preserve a useful ductility is, in fact, one of the factors most limiting to the quality, or extent of, superelasticity. Conversely, we could say that an inherently more ductile Ni-Ti alloy would allow us to further enhance its superelastic character.

Although we have concentrated on the width of the superelastic window, a few words on some other aspects are in order. As we reduce the annealing temperature (increase strength) the superelastic plateau becomes flatter. Also, since M_s is decreased, the window is shifted to lower temperatures. We should also note that all of the above figures depicted binary Ni-Ti that was cold worked 40%. Decreasing the amount of cold work is exactly equivalent to increasing the annealing temperature, thus the detailed effects of cold working will not be presented. The effect of annealing time, however, is more complex. While it is true that shorter times are generally equivalent to lower temperatures, the effect is not straightforward. There appears to be a step in the strength/time curve.

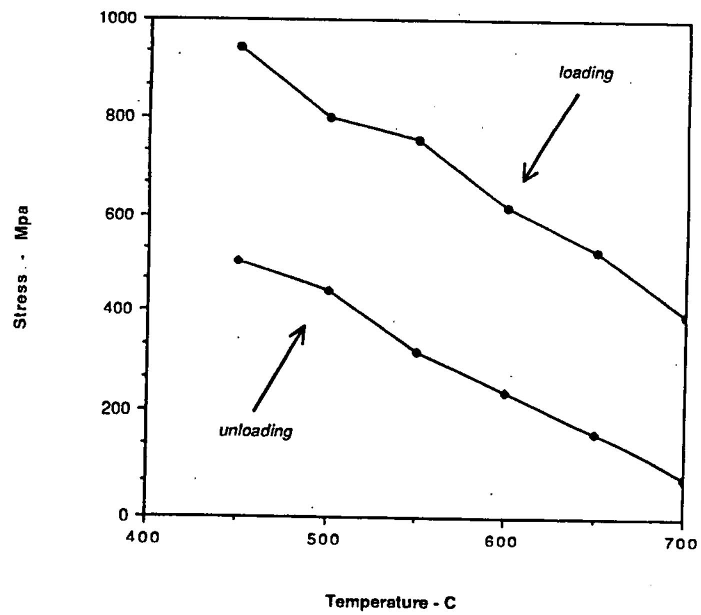

Figure 19 Superelastic plateau stresses shown as a function of the annealing temperature; note that the stress hysteresis decreases with increasing annealing temperature, in good agreement with figure 16. The alloy is as described in Figure 15.

Very short times at high temperatures appear to maintain high strength without increasing M_s and without bringing out the R phase. While these short (under 5 minute) heat treatments are usually impractical in the production of anything except straight wire, they do tend to lead to somewhat superior superelastic behaviors.

3.2 Aging

As pointed out earlier in these proceedings[27], Ni-rich Ni-Ti alloys decompose during aging through a series of more stable compounds: $Ni_{14}Ti_{11}$, Ni_4Ti_3, Ni_3Ti_2 and finally Ni_3Ti. These precipitates strengthen the Ni-Ti matrix, which enhances superelasticity but also cause a shift in the transformation temperatures[28]. Many of these effects are complex, but to illustrate general trends we will follow the aging of a Ni-Ti wire with 50.8 atomic percent Ni after solution treating at 850°C and water quenching. To simplify matters, we have chosen an aging temperature of 325°C and will not consider that to be a variable.

The shifts in the transformation temperatures during aging are shown in Figure 20. M_s increases steadily while A_f initially drops then again rises. The R-phase becomes evident after the first minute of aging, then R_s climbs rather quickly to nearly 60°C. On this basis alone one would expect room temperature superelasticity after aging one minute, and for superelasticity to disappear again after 100 minutes - at this point R_s

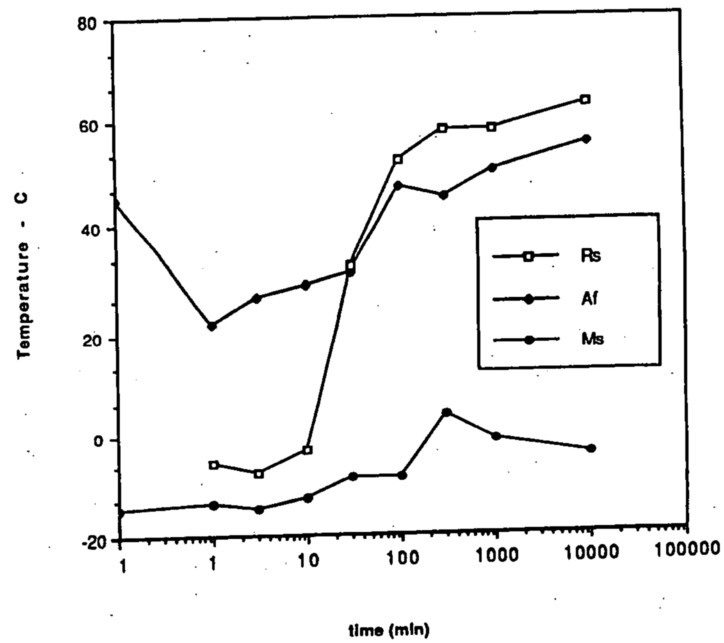

Figure 20: Aging effects on transformation temperatures are shown in a Ni-Ti wire with 50.8% Ni. The wire was annealed for 30 minutes in vacuum at 850°C and quenched in water prior to aging at 350°C for the time shown on the ordinate. Note that the reported transformation temperatures are under a 150 MPa stress.

would be above ambient. Figure 21 shows that the austenite is strengthened by aging, but the maximum strength levels are only moderate, and start to increase after 10 minutes. Also shown in Figure 21 is the dependence of stress rate upon aging time, showing a sharp reduction until about the 10 minute mark. If one compares the requirements of superelasticity discussed in section 3.0 with Figures 20 and 21, one would conclude that optimum superelasticity should be found after aging times of 10 to 100 minutes. Figures 22 and 23 verify this.

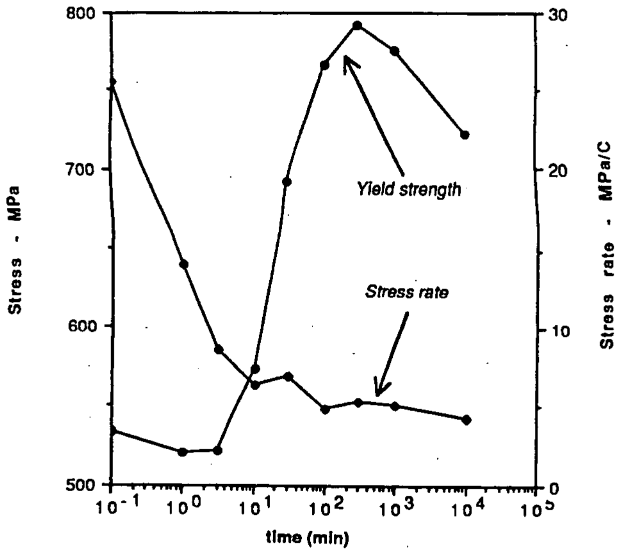

Figure 21 Age hardening of the wire described in the caption of Figure 20 is shown. Note that the stress rate change is marked and generally opposite to the resistance to slip.

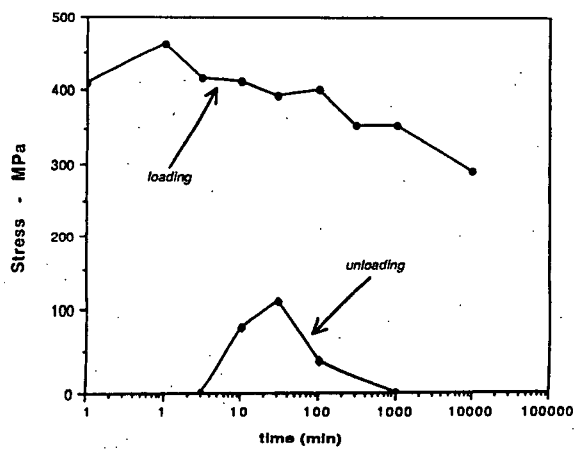

Figure 22 The loading and unloading plateau stresses are plotted as function of aging time, showing a general decrease in loading stiffness (commensurate with Figure 20), and a superelastic plateau that is only observable after 10 to 100 minutes of aging. The wire is again that described in the caption of Figure 20.

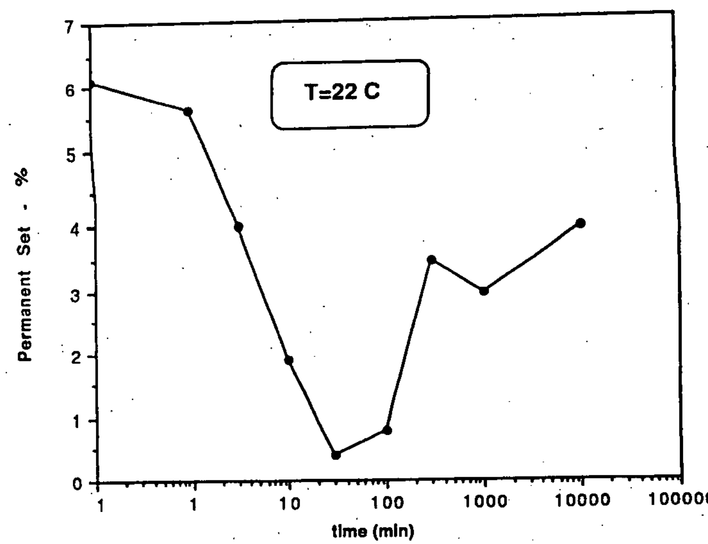

Figure 23 Aging effects on permanent set in the same wire described in Figure 20, again indicating superelastic effects only between 10 and 100 minutes of aging.

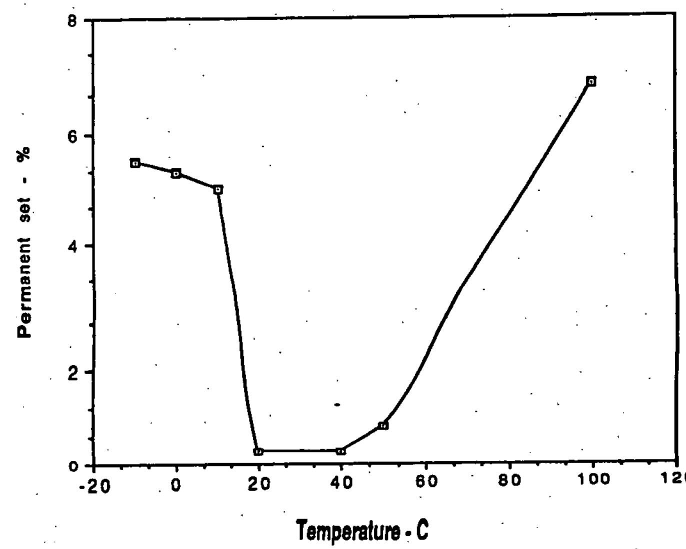

Figure 24 A more detailed look at the superelastic temperature window of a Ni-Ti wire with 50.8% Ni after aging 30 minutes at 350°C. The window is only 30°C wide.

Figure 22 shows the loading plateau is relatively constant (the slight decrease being commensurate with the increasing M_S in Figure 20), and that the unloading plateau stress reaches a maximum after 30 minutes of aging. With times less than 3 minutes, no unloading plateau is found. Figure 23 shows that the room temperature permanent set reaches a marked minimum between 30 and 100 minutes. Finally we can look at permanent set as a function of temperature (Figure 24). The window is substantially narrower than in the cold worked binary shown in Figure 12, but that is expected since the austenitic strength levels in the aged material are substantially lower.

Whether the aging or the cold working approach is better depends strongly upon application specifics. Generally speaking it is possible to achieve superelasticity with lower strength levels and greater ductilities through aging, but the windows are narrower. The material shown in Figure 24 exhibited over 60% elongation to failure; the material of Figure 12 only 10%. Also, the constant stress plateaus are longer and flatter in the aged material as a rule. Finally, greater stiffness can be obtained at room temperature in the cold worked material.

The above example is only that: an example. In alloys of greater Ni content, aging effects can be substantially faster and strengths higher. Also at higher temperatures aging can be more rapid. Still the trends are valid and can be generally applied. The choice of an optimum aging temperature may also depend upon the exact alloy and condition - Miyazaki et al[29] aged a 50.6% Ni alloy at 300, 400 and 500°C and concluded that 400°C was optimum. More recent work [30] suggests that better properties can be obtained by aging at 325°C to 350°C.

3.3 Compositional effects

Binary Ni-Ti alloys are limited to superelastic applications at room temperature and above - and at room temperature, their usefulness is quite limited by the rather low unloading stress plateau level. The reason is that it is difficult to lower A_f below room temperature while maintaining a high austenitic strength. To understand this, recall that to achieve a low M_s one goes to the Ni-rich side of the phase diagram. Here M_s is indeed decreased after quenching; but the alloys also become susceptible to aging effects which increase the transformation temperatures. In order to obtain the austenitic strength levels required for superelasticity, one must age the Ni-rich alloys, even if inadvertently during the recovery anneal following cold working. In addition to increasing M_s, aging introduces the R-phase and increases hysteresis. Thus room temperature represents a practical lower limit for superelasticity in binary Ni-Ti.

To obtain superelastic windows at low temperatures, or to increase the stiffness at room temperature, two alloying strategies have been used. The first is to add an M_s suppressing addition[31] such as vanadium, cobolt, iron, aluminum or chromium. In proper proportions these additions suppress M_s without causing an instability to aging. Thus the cold working approach to increasing strength can be invoked while keeping both M_s and R_s below room temperature. An example of the benefits of such a modified alloy are shown in Figure 25: here the vanadium alloy is clearly stiffer

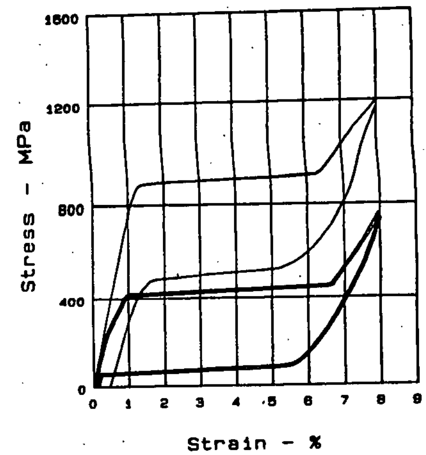

Figure 25 Third element additions such as vanadium suppress M_s and can lead to far greater superelastic stiffnesses and energy storage abilities. The case shown here is a Ni-Ti wire with 6 at.% V after cold working 40% and annealing at 500°C for one hour. The energy storage efficiency is more than 5 times that of the binary.

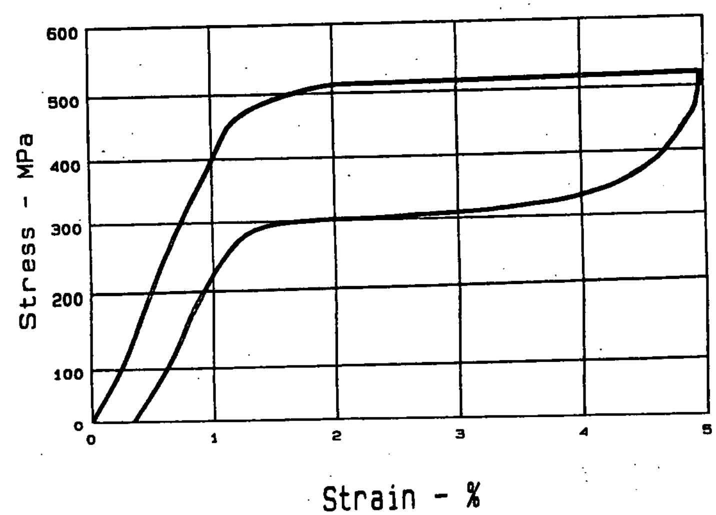

Figure 26 An extreme example of low temperature superelastic windows is illustrated by this Ni-Ti-Fe rod deformed at -196°C and still showing excellent superelasticity.

(higher unloading plateau stress) than the binary. In this case the stored energy effeciency is more than 5 times that of the binary. A still more exaggerated case is shown in Figure 26, where a Ni-Ti-Fe alloy is shown to be fully superelastic even at -196°C. Some care must be taken, however, since these doped alloys are often less ductile than the binaries. The second alloying approach is to add copper[32]. Copper has the advantage of reducing hysteresis and eliminating the R-phase. There is, however, little in the way of quantitative design data for these alloys.

4. Summary:

We have presented here an overview of pseudoelasticity, and more specifically of superelasticity in Ni-Ti. The key engineering parameters (stiffness, hysteresis, permanent set and stored energy) have been defined, showing that Ni-Ti has the theoretical capability of reducing the size and weight of springs by nearly an order of magnitude. The value of Ni-Ti in any particular application must be judged, however, with an understanding of what temperature variations are expected. Two approaches to producing superelasticity were presented: cold working and aging. Which may be preferred in a particular case would depend upon the alloy composition, the shape of the device to be made, and the properties desired.

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